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Effects of Gamma Radiation on Polymers in Solutions. (VII)

Effects of Degree of Polymerization on Crosslinking of Poly(Vinyl Alcohol) in Aqueous Solutions

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Dilute aqueous solutions of poly(vinyl alcohol) having various degrees of polymerization from 60 to 19700 were exposed to gamma radiation in the absence of air and the crosslinking mechanism was examined in detail. It was found from the results that the critical concentration for gel-formation $C_{crit.}$ can be written by the following equation:

$$C_{crit.}[\eta]^{0.62} = \text{const.}$$

where $[\eta]$ is the limiting viscosity number of unirradiated samples. The assumption that at the critical concentration the polymer spheres just begin to overlap with each other and array in the order of closed packing could give a satisfactory account of the experimental results. Namely, the radius of polymer sphere calculated on the basis of the above assumption was almost proportional to the hydrodynamic effective radius calculated from the Einstein formula and radius of gyration. The rapid rise of gelation dose usually observed near the critical concentration may be due to slight change in the degree of overlapping of polymer coils. The gelation dose at a fixed concentration was inversely proportional to the degree of polymerization of samples used. G-value for crosslinking was found to be 6.2. The indirect effect via water was quantitatively discussed and it was found that only 5.5% of radiation energy absorbed directly by water was actually dissipated for the formation of crosslinking.

INTRODUCTION

During the course of a continuing program of study concerning the radiation-induced crosslinking of polymers in aqueous solution¹⁻⁵⁾, it was found to be very likely that the critical concentration for gel-formation corresponds to the polymer concentration where the polymer spheres just begin to be in contact with each other. If this is true, the size of the polymer sphere will be able to be calculated using the data concerning the crosslinking in solutions. In the previous works^{3,5)}, the expansion of polyions was calculated briefly for various charge densities and added salt concentrations. In the case of polyelectrolytes, however, the quantitative treatment of experimental results was not easy, since the crosslinking was largely influenced by the electrostatic repulsive forces arising from the ionized side groups.

The present work is an extension of previous investigations, with attention being focussed in the effect of size of polymer coil on the crosslinking in dilute aqueous solutions. The sample used here is poly(vinyl alcohol) (PVA) with

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various degrees of polymerization from 60 to 19700. In addition to the estimation of the radius of polymer sphere, the contribution of water to the crosslinking of polymer was quantitatively discussed.

EXPERIMENTAL

1) Material

Initial degrees of polymerization and limiting viscosity numbers $[\eta]$ of PVA used are shown in Table 1. The preparative method of original poly(vinyl

Table 1. Characteristics of Samples and Polymerization Condition of Original PVAc.

| Sample | $[\eta]_{\text{H}_2\text{O}}$ | \bar{P} | Polymerization condition of original PVAc | | | |
|--------|-------------------------------|-----------|---|-------------------|---------------------|------------|
| | | | Solvent | Monomer conc. (%) | Initiator conc. (%) | Temp. (°C) |
| I-1 | 2.7 | 19700 | Bulk | | γ -ray | -78 |
| S-2 | 1.9 | 10500 | " | | " | " |
| N-1 | 1.48 | 4000 | Commercial product | | | |
| L-8 | 1.06 | 2350 | Bulk | | AIBN 0.1 | 30 |
| F-5 | 0.80 | 1500 | Ethyl acetate | 60 | BPO 0.05 | 75 |
| N-2 | 0.380 | 470 | Commercial product | | | |
| M-3 | 0.212 | 190 | Ethanol | 30 | BPO 0.1 | 60 |
| M-5 | 0.128 | 86 | " | " | " " | " |
| M-6 | 0.094 | 60 | " | " | " " | " |

acetate) (PVAc) is also tabulated there. Samples I, S, L and F were obtained by re-saponification of fractionated linear PVAc, and samples N and M by fractionation of PVA. The degree of saponification was in all cases approximately 100%. The polymers obtained were purified several times by precipitation from aqueous solutions with methanol or acetone and by extraction by methanol in a Soxhlet extractor for 8 hrs. After drying under vacuum at 50°C, they were stored over P_2O_5 .

The degree of polymerization \bar{P} was calculated from the equation: $[\eta] = 7.51 \times 10^{-3} \times \bar{P}^{0.64}$ (in water, 30°C)⁶⁾ except for samples of I-1 and S-2. For these two samples, the equation could not be used, since \bar{P} 's of these polymers were too high for the equation to be applied. Therefore, they were estimated indirectly assuming that \bar{P} 's of these samples were precisely equal to those of PVAc, which was obtained by acetylation of these PVA. The value of \bar{P} of these acetylated PVA was calculated from the following equation: $[\eta] = 8.91 \times 10^{-3} \times \bar{P}^{0.62}$ (in acetone, 30°C)⁶⁾.

2) Irradiation Procedure and Determination of Gel Point

They are similar to those described previously⁴⁾. The temperature during irradiation was about 20°C and the dose rate was 1.45×10^5 r/hr. All solutions before irradiation were quite transparent. Irradiation was carried out in the absence of air in all cases.

RESULTS AND DISCUSSION

1) Effects of Degree of Polymerization and Concentration on Gelation

Minimum dose needed for incipient gelation, *i.e.*, gelation doses, are plotted in Fig. 1 against the polymer concentration for the samples having various initial degrees of polymerization. Evidently, all the curves in Fig. 1 have the

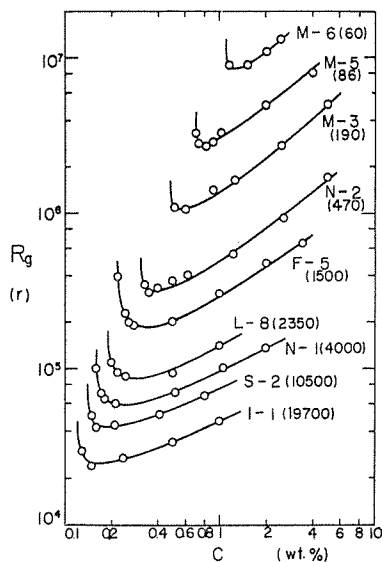


Fig. 1. Influence of polymer concentration C and degree of polymerization on gelation dose R_g for PVA irradiated in deaerated aqueous solutions. The number in parentheses represents the initial degree of polymerization.

similar shape to those⁷⁾ found out when polymers of crosslinking type were irradiated in aqueous solutions; beyond a certain concentration gelation abruptly occurs, and the gelation dose decreases very sharply with the concentration and then after reaching a minimum it increases again rather slowly. The critical concentration, below which gel cannot be formed however large a dose is used,

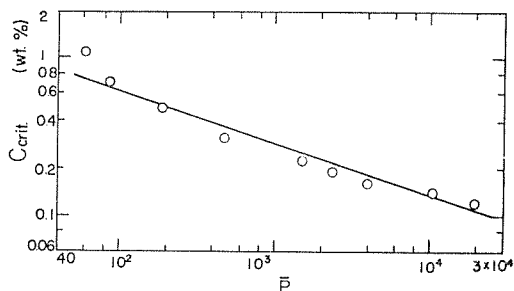


Fig. 2. Relation between critical concentration $C_{crit.}$ for gel-formation and initial degree of polymerization \bar{P} .

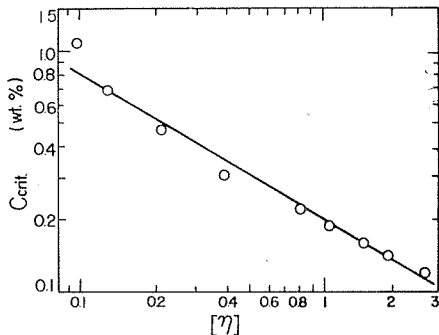


Fig. 3. Relation between critical concentration $C_{crit.}$ for gel-formation and initial limiting viscosity number $[\eta]$.

seems to be somewhat ambiguous from the shape of curves in Fig. 1. However, they could be determined very definitely since the solutions never exhibited gelation when irradiated at the concentrations of only 0.01% lower than the critical concentration. At such low concentrations, the irradiated solutions were turbid irrespectively of the degree of polymerization of the samples used, indicating the formation of intra-molecular crosslinking.

The critical concentration as a function of degree of polymerization and limiting viscosity number of unirradiated PVA is shown in Figs. 2 and 3, respectively. The dependence appears in either case to be linear as a first approximation. The relatively large deviation of plots for M-6 sample may be ascribed to its being roughly fractionated because of the final fraction.

The linear relation observed in Fig. 3 can be given by

$$C_{crit.}[\eta]^{0.62} = 0.2 \quad (1)$$

where $C_{crit.}$ is the critical concentration for gel-formation and the polymer concentration is expressed in g/100 cc unit. Now, we will discuss briefly the equation (1). Similarly to the treatment in the previous papers^{3,5)}, we will regard the polymer coil in dilute solutions as a sphere. On assuming that these spheres exist in solutions in the close-packed structure, the average distance R_{12} between two molecular centers at a polymer concentration C and for a molecular weight M is:

$$R_{12} = \left(100 \frac{M}{CN} \sqrt{2} \right)^{1/3} \quad (2)$$

where N is Avogadro's number. For $C = C_{crit.}$, $R_{12} = 2R_e$, where R_e is the radius of the polymer molecule, hence

$$C_{crit.} = \frac{100\sqrt{2}}{8N} \frac{M}{R_e^3} \quad (3)$$

The limiting viscosity number $[\eta]$ may be regarded as a measure of the ratio of the effective hydrodynamic volume V_e ($V_e \propto R_h^3$) of the polymer to its molecular weight; that is,

$$[\eta] \propto \frac{R_h^3}{M} \quad (4)$$

And the $[\eta]-M$ relation for PVA in aqueous solutions has been determined as

$$[\eta] \propto M^{0.64} \quad (5)$$

Then, by combining (1), (3), (4) and (5), we find that

$$R_e \propto M^{0.47} \quad (6)$$

$$R_h \propto M^{0.55} \quad (7)$$

Both equations indicate that the radius is nearly proportional to the square root of the molecular weight.

2) Dimension of PVA Molecule in Aqueous Solution

If it can be taken for granted that the main-chain scission occurs to a negligible extent during irradiation, the radius of PVA in solution can be evaluated

from the equation (3). The possibility of scission is, now, supposed to be quite negligible because the doses used here are much smaller by a factor of several tens than those required to degrade solid PVA detectably⁸⁾. Furthermore, the facts that, in the present case, air is eliminated completely from the solution, and that the rise observed in the curves in Fig. 1 is in all cases very sharp, may provide also a support for the absence of the scission. Dieu⁹⁾, also concluded that degradation did not occur, based on the viscosity change of PVA solutions irradiated under the same condition as ours.

By rewriting (3), we obtain

$$R_c = 10.89 \left(\frac{\bar{P}}{C_{crit.}} \right)^{1/3} \quad (8)$$

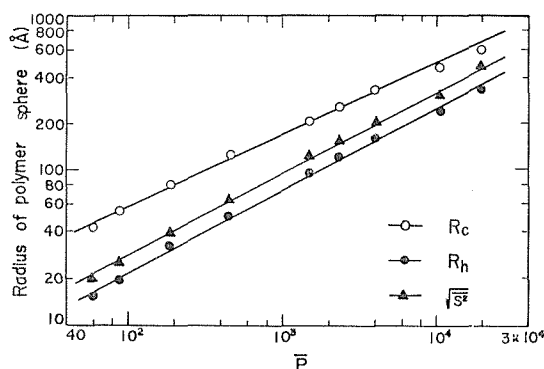


Fig. 4. Radius of polymer sphere calculated from the data of the cross-linking and viscosity.

where R_c is expressed in Å. Fig. 4 is a double logarithmic plot of the radius of the polymer sphere calculated from equation (8) against degree of polymerization. For comparison, radius of gyration $\sqrt{S^2}$, and hydrodynamic effective radius R_h were also plotted. As can be seen from Fig. 4, R_c would be said to have about the same order of magnitude as that of R_h and $\sqrt{S^2}$.

3) Mechanism of Crosslinking in Solutions

The radius of polymer sphere calculated by regarding the critical concentration as the minimum concentration, at which overlapping of polymer coils begins, was nearly proportional to the hydrodynamic radius. This fact may give a certain evidence for the assumption concerning the significance of the critical concentration. It is probably because the meaning of the critical concentration has not been made clear that a satisfactory explanation has not been given concerning the mechanism of crosslinking in dilute solutions up to date. If the critical concentration can be regarded as the minimum concentration of overlapping as described above, the anomalous concentration dependence on crosslinking observed in Fig. 1 can be explained by the following simple mechanism. We will treat, in the present paper, mainly the crosslinking occurring in the concentration range above $C_{crit.}$, and the details as to the crosslinking below $C_{crit.}$ will be presented in the subsequent paper.

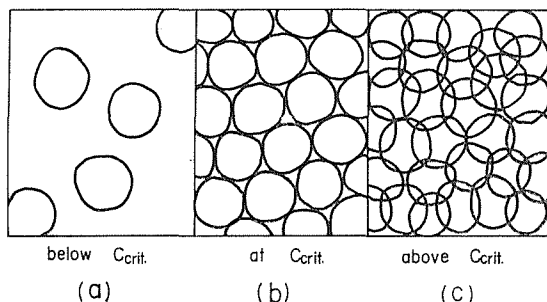


Fig. 5. Relative location of polymer spheres in solutions.

When the crosslinking mechanism in aqueous solutions is concerned, the indirect effect due to water should be taken into account, first of all. However, as the concentration of the solutions become relatively low, contact or overlapping of polymer coils may become a more important factor for crosslinking than the indirect effect. In Fig. 5a schematic representation of the relative location of each polymer sphere in solution is given. When the concentration is so low that the sphere can not interfere each other as is illustrated in Fig. 5(a), the formation of three-dimensional net-work gel will be impossible undoubtedly. In the case of a moderately concentrated solution as is shown in Fig. 5(b), where all polymer spheres just are in contact with each other in the solution, a continuous macro-gel can be formed. The concentration at this point corresponds to $C_{crit.}$. As the solution becomes more highly concentrated as shown in Fig. 5 (c), the effect of overlapping will be less important than the indirect effect as far as the concentration dependence is concerned, because the inter-molecular crosslinking can occur readily in this case. The influence of this overlapping on the crosslinking solutions is shown qualitatively by a curve (a) in Fig. 6. For convenience, we used the gelation dose as a measure of the rate of crosslinking.

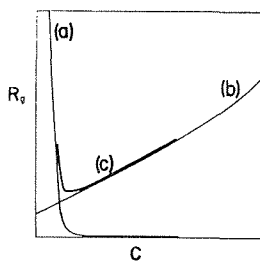


Fig. 6. Schematic representation of concentration dependence of the overlapping effect (a) and the indirect effect (b). (c) represents the resultant effect of these two factors.

Next, we will consider by what type of reactions the crosslink is formed. We have found, in the previous studies^{3,10)} on the radiation-induced crosslinking of various polymers, that $H\cdot$ and $OH\cdot$ produced by the action of radiation on water play an important role at the crosslinking reaction. Namely, the crosslinking may be formed partly by coupling of two polymer radicals which are

produced as a result of hydrogen abstraction from the polymer chain by $\text{H}\cdot$ and $\text{OH}\cdot$. The reaction scheme is then :



where P represents the polymer molecule. In addition to these reactions, the crosslinking may be partly formed by the reaction of $\text{P}\cdot$ produced from polymers by the direct action of radiation :



The formation of crosslinking through the reactions (9) to (12) is generally called "indirect effect", and that through (13) and (14) "direct effect". Obviously, the indirect effect depends on the polymer concentration, while the direct effect does not. It has been generally accepted that in dilute solutions the direct effect is almost negligible compared with the indirect effect. The concentration dependence on the indirect effect will be shown qualitatively by a curve (b) in Fig. 6. The steady increase of the gelation dose with increasing polymer concentration is due to the decreasing amount of $\text{H}\cdot$ and $\text{OH}\cdot$ per polymer molecule.

Combining those two curves of (a) and (b), one can obtain a curve quite similar to those in Fig. 1. This indicates that the crosslinking in aqueous solutions is strongly influenced by the degree of overlapping of the polymer coil in the neighborhood of $C_{crit.}$, whereas in the more concentrated solution it depends exclusively on the indirect effect. It is, of course, very likely that, besides these two effects, there may be a few factors influencing the concentration dependence on crosslinking. Main factors among them may be the mobility of polymer segments and the dimension of polymer coils. However, these concentration dependences are supposed to be negligible compared with that of the indirect effects, for the high concentration range.

4) Indirect Effect

Although it is very important to estimate the indirect effect quantitatively, only few attempts^{1,11)} have been done probably because of the uncertainty of the mechanism of reactions which are closely related to the indirect effect. In order to avoid difficulties in calculation, we will discuss, here, the crosslinking occurring in the concentration range relatively higher than the $C_{crit.}$, since near the $C_{crit.}$ such factors as the degree of overlapping should be taken into account. We shall make the assumptions: (1) polymer coils "drain through" each other so that the segment distribution is uniform, (2) the formation of intra-molecular crosslinking can be neglected, (3) the energy absorbed directly by the polymer molecule is completely used for the crosslinking and (4) the energy transfer does not occur.

Let c be the polymer concentration expressed in weight %, and R the radia-

tion dose in roentgen unit. Then, for 100 grams of the solution, the energy absorbed by the polymer is RAc and the energy absorbed by water is $RA(100-c)$. A is the conversion-factor from roentgen unit to e.v. ($A=0.58 \times 10^{14}$ e.v./r.g.). It seems very plausible that the energy absorbed in water, *i.e.*, $RA(100-c)$ is used for the crosslinking not completely, but only partly. Then, the total energy actually dissipated for the crosslinking is given by

$$E = RAc + kRA(100-c) \quad (15)$$

where k is assumed tentatively to be independent of c . The first term in the right side of the equation (15) is related to the direct effect, and the second term to the indirect effect. The number of polymer molecules which are present in 100 grams of the solution, is cN/M , so that the energy per polymer molecule is

$$\epsilon = \frac{RAc + kRA(100-c)}{cN/M} \quad (16)$$

Therefore, if we define the energy required for the formation of a crosslink as E_c , the number of crosslinks per polymer molecule is

$$\delta = \frac{RAc + kRA(100-c)}{cNE_c/M} \quad (17)$$

According to the theories proposed by Stockmayer¹²⁾ and Charlesby¹³⁾, the incipient gelation occurs when there is one crosslink per two initial molecules and when they have initially a uniform molecular weight distribution; that is

$$\delta = 0.5 \quad (18)$$

Thus, if the gelation dose is denoted by R_g , we find that

$$1/R_g = 2AM/NEc(100k/c + 1 - k) \quad (19)$$

or,

$$1/R_g P = AM_0/50NG_c(100k/c + 1 - k) \quad (20)$$

where M_0 is the molecular weight of the monomer unit and G_c is the G -value for crosslinking, in other words, the number of crosslinks formed per 100 e.v. of energy. The equation (20) indicates that R_g is inversely proportional to P of

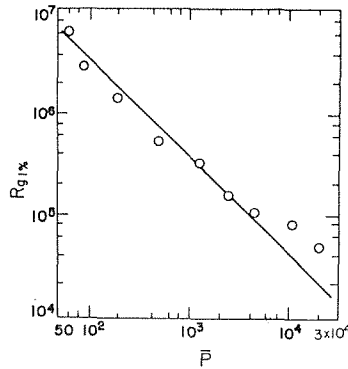
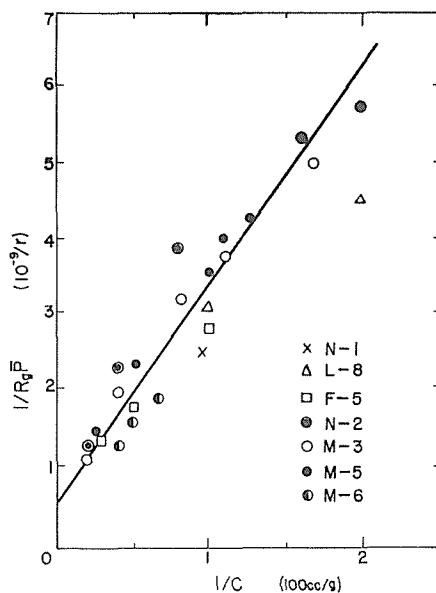


Fig. 7. Influence of initial degree of polymerization on gel-formation of PVA irradiated in 1.0% solutions.


 Fig. 8. Plot of $1/R_g\bar{P}$ against $1/c$ for various PVA.

the samples, if $c = \text{const.}$ As can be seen from Fig. 7, which is a double logarithmic plot of R_g at the 1.0% solution against \bar{P} , the relation $R_g \propto 1/\bar{P}$ is obtained as expected. Furthermore, according to the equation (20), the plot of $1/R_g\bar{P}$ against $1/c$ should give a straight line. By applying this equation to the data in Fig. 1, we obtain a straight line shown in Fig. 8 in good agreement with the theory. From these results, the above assumption that k is independent of c , is found to be true. The slope and the intercept of this straight line show that $G=6.2$, $E_e=16$ e.V. and $k=0.055$.

We shall define the fraction of indirect effect $f_{in.}$ as follows,

$$f_{in.} = \frac{\text{indirect effect}}{\text{direct effect} + \text{indirect effect}} \quad (21)$$

Then, we obtain

$$f_{in.} = \frac{k(100-c)}{c+k(100-c)} \quad (22)$$

By substituting $k=0.055$ into the equation (22), and plotting $f_{in.}$ against the

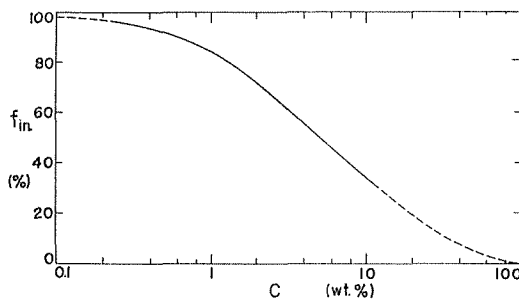


Fig. 9. Dependence of indirect effect on polymer concentration.

polymer concentration according to the equation (22), we obtain a curve shown in Fig. 9. It indicates clearly that the indirect effect is very important in the low concentration range, while in the highly concentrated solution the direct effect becomes more prominent. Hitherto, this feature generally observed pertaining to the crosslinking and degradation in aqueous solutions has been described only qualitatively.

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